

# Adsorbed states of a long - flexible polymer chain

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A phase diagram for a surface-interacting long flexible polymer chain in a two-dimensional poor solvent where the possibility of collapse exists is determined using exact enumeration method. A model of a self-attracting self avoiding walk (SASAW) on a square lattice was considered and up to 28 steps in series were evaluated. A new adsorbed state having the conformation of a surface attached globule is found. Four phases (i) desorbed expanded, (ii) desorbed collapsed, (iii) adsorbed expanded and (iv) surface attached globule are found to meet at a point on the adsorption line.

64.60.-i, 68.35.Rh, 5.50.+q

The behaviour of a long flexible polymer chain near an impenetrable surface is a subject of considerable experimental and theoretical importance [1–3]. This is because such a chain may exhibit a phase diagram characterized by many different universality domains of critical behaviour. The subtle competition between the gain of internal energy and corresponding loss of entropy at the surface may lead to the possibility of the coexistence of different regimes and multicritical behaviour. An attracting surface may lead adsorption - desorption transition from the state when the chain is mostly attached to the surface, to the state of detachment when the temperature is increased. This behaviour finds applications in lubrication, adhesion, surface protection etc.

The essential physics associated with the behaviour of a surface interacting polymer chain in a good solvent where monomer-solvent attraction is greater than the monomer-monomer attraction, is derived from a model of self-avoiding walk (SAW) on a semi-infinite lattice. If the surface is attractive, it contributes an energy  $\epsilon_a$  ( $< 0$ ) for each step of the walk along the lattice boundary. This leads to an increased probability characterized by the Boltzmann factor  $\omega = \exp(-\epsilon_a/k_\beta T)$  of making a step along the wall, since for  $\epsilon_a < 0$ ,  $\omega > 1$  for any finite temperature  $T$  ( $k_\beta$  is the Boltzmann constant). Because of this the polymer chain becomes adsorbed at low temperatures on the surface while at high temperatures all polymer conformations have almost same weight and non adsorbed (or desorbed) behaviour prevails. The transition between these two regimes is marked by a critical adsorption temperature  $T_a$ , with a desorbed phase for  $T > T_a$  and adsorbed phase for  $T < T_a$ . At  $T = T_a$  one may define the crossover exponent  $\phi$ , as  $M \sim N^\phi$ , where  $N$  is the total number of steps and  $M$  the number of steps on the surface. The transition point  $T_a$  is a tricritical point [3]. Both the surface and the bulk critical exponents have been calculated using renormalization group methods [4], exact enumeration methods and Monte-Carlo simulations [5–8]. For a two dimensional system exact values of the exponents have been found by using conformal invariance [9].

The situation, is, however, different when the sur-

face interacting polymer chain is in a poor solvent where monomer-monomer attraction dominates over the monomer-solvent attraction. As is well known, a long-flexible polymer chain in a poor solvent exhibits a transition from a compact globule (collapsed state) to a expanded state when the temperature is increased. Above the critical  $\theta$  temperature (often referred to as the  $\theta$ -point) the chain behaves as it would in a good solvent and below this temperature it behaves like a compact globule. At the  $\theta$ -point the chain behaviour is described by a tricritical point of the  $O(n)$  ( $n \rightarrow 0$ ) spin system [10]. However, when the chain is in the vicinity of an impenetrable surface the competition between the monomer-monomer attraction and the surface-monomer interaction gives rise to many new features. Attempts have been made to study these features using several approaches [3,7,8,11].

For two-dimensions the transfer matrix method has been used for a directed polymer chain [12] whereas for the nondirected (isotropic) version the exact enumeration method has been used [8]. In both cases, three phases, desorbed expanded, desorbed collapsed and a single adsorbed phase have been predicted. However, the true nature of the phase diagram remained unknown. For three dimensions, the Monte-Carlo simulations method [13] has been used for a finite length ( $\sim 100$ ) chain which led to a phase diagram containing four phases; desorbed expanded (DE), desorbed collapsed (DC), adsorbed expanded (AE) and adsorbed collapsed (AC). The phase diagram shows a phase boundary between the AE and DC phases leading to two points on the phase diagram where three phases coexists(triple point). However, the phase diagram found by the exact enumeration technique [14] has many features which are different from that found in ref. [13]. This indicates the possibility of a richer phase diagram than has been realized so far. In view of this we reexamine the problem of simultaneous adsorption and collapse of a linear polymer chain on a square lattice and investigate the phase diagram and critical parameters using the exact enumeration technique. We prefer this technique because in this case the scaling corrections are correctly taken into account by a suitable extrapolation scheme. As shown by Grassberger and Hegger [5], to

achieve the same accuracy with the Monte Carlo method one has to consider a polymer chain of about two orders of magnitude longer than in the exact enumeration method.

We consider SASAW on a square lattice restricted to half space  $Z \geq 0$  (impenetrable hard wall). Walk starts from the middle of the surface. Let  $C_{N,N_s,N_m}$  be the number of SAWs with  $N$  steps, having  $N_s$  ( $\leq N$ ) step on the surface and  $N_m$  nearest neighbor. We have obtained  $C_{N,N_s,N_m}$  for  $N \leq 28$  for square lattice by exact enumeration method.

Now we consider the interaction energy  $\epsilon_a$  associated with each walk on the surface and  $\epsilon_m$  for monomer-monomer interaction. Partition function of the attached chain is

$$Z_N(\omega, u) = \sum_{N_s, N_m} C_{N,N_s,N_m} \omega^{N_s} u^{N_m} \quad (1)$$

where  $\omega = e^{-\epsilon_a/kT}$  and  $u = e^{-\epsilon_m/kT}$ .  $\omega > 1$  and  $u > 1$  for attractive force. Reduced free energy for the chain can be written as

$$G(\omega, u) = \lim_{N \rightarrow \infty} \frac{1}{N} \log Z_N(\omega, u) \quad (2)$$

In general it is appropriate to assume that as  $N \rightarrow \infty$

$$Z_N(\omega, u) \sim N^{\gamma-1} \mu(\omega, u)^N \quad (3)$$

where  $\mu(\omega, u)$  is the effective coordination number and  $\gamma$  is the universal configurational exponents for walks with one end attached to the surface. The value of  $\mu(\omega, u)$  can be estimated using ratio method [15] with associated Neville table. From equations (2) and (3) we can write

$$\log \mu(\omega, u) = \lim_{N \rightarrow \infty} \frac{1}{N} \log Z_N(\omega, u) = G(\omega, u) \quad (4)$$

$Z_N(\omega, u)$  is calculated from the data of  $C_{N,N_s,N_m}$  using equation (1) for a given  $\omega$  and  $u$ . From this we construct linear and quadratic extrapolants of the ratio of  $Z_N(\omega, u)$  for the adjacent values of  $N$  as well as the alternate one. Results for alternate  $N$  give better convergence. When  $u = 1$  and  $\omega = 1$  the value of  $\mu$  is found to be 2.638 which is in very good agreement with the value given in ref. [2,7].

The value of  $\omega_c(u)$  at which polymer gets adsorbed for a given value of  $u$  is found from the (i) plot of  $G(\omega, u)$  which remains fairly constants until  $\omega = \omega_c$  and increases consistently as a function of  $\omega$ , for  $\omega \geq \omega_c$  (ii) from the plot of  $\partial^2 G(\omega, u)/\partial \epsilon_a^2$  at constant  $u$  and (iii) from the plot of  $\gamma^0 - \gamma_1$  (see Eq.(6) and discussions which follow it) as a function of  $\omega$  for different  $N$ . The value of  $\omega_c$  found from the plot of  $G(\omega, u)$  is slightly lower than the peak value of  $\partial^2 G/\partial \epsilon_a^2$ . It is, however, observed that as  $N$  is increased from 22 to 28 the peak value shifts to smaller  $\omega$  and appears to converge on the value of  $\omega$  found from  $G(\omega, u)$  plot. We therefore choose the value of  $\omega_c$  found from the plot of  $G(\omega, u)$  and determine lines  $\omega_c(u)$  and

$\omega_{c1}(u)$  (see Fig.1) by this method. For  $u = 1$ , the value of  $\omega_c$  is 2.050 which is in very good agreement with the value ( $= 2.044 \pm 0.002$ ) reported in ref. [8]. Similarly the phase boundary separating the extended and collapsed phases is calculated from the plot of  $G(\omega, u)$  as a function of  $u$  for a given  $\omega$ . However, transition point  $u_c$  is located more accurately from the peak of  $\partial^2 G(\omega, u)/\partial \epsilon_m^2$  at constant  $\omega$ . For  $\omega = 1$ , the value of  $u_c$  is 1.93 which is in good agreement with the value found by Foster et al [8] and the Monte Carlo results ( $= 1.94 \pm 0.004$ ) [5]. The method is found to work for all values of  $\omega$  i.e in both the bulk and the adsorbed regimes. However, as  $\omega$  is increased the values of  $G(\omega, u)$  do not remain as smooth as at lower values of  $\omega$ , therefore introducing some inaccuracy in the value of  $u_c$ . The estimate of this inaccuracy is of the order of 5% for  $\omega > 4$ . We therefore conclude that the  $u_c$  and  $\omega_{c2}$  (Fig.1) lines are determined with reasonable accuracy.

The surface critical exponent  $\gamma_1^{N,k}$  can be calculated using the relation:

$$\gamma_1^{N,k} = \frac{\log(Z_N/Z_{N-2}) - k \log(\mu)}{\log(N/(N-k))} + 1 \quad (5)$$

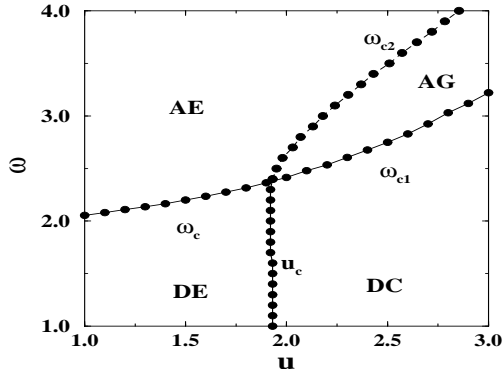
where subscript “1” indicates the corresponding quantity of the surface (with one end of the polymer is attached to the surface). If we assume that  $\mu$  does not depend on  $\omega$  and polymer is in desorbed phase, then we can calculate the quantity  $\gamma^0 - \gamma_1$  from the above equation

$$\gamma^0 - \gamma_1 = \frac{\log(Z_N^0 Z_{N-2}/Z_{N-2}^0 Z_N)}{\log(N/N-2)} \quad (6)$$

where superscript “0” indicates the corresponding quantity of the bulk (i.e without surface). In this case one calculates  $\gamma^0 - \gamma_1$  for different  $N$  using above equation and plot it as a function of  $\omega$ . The location of adsorption point  $\omega_c$  can be determined from the intersection of successive approximation to  $\gamma^0 - \gamma_1$  in the limit  $N \rightarrow \infty$ . This method, however, fails beyond the  $\theta$ -point and reproduces closely the adsorption phase boundary below the  $\theta$ -point found by the method discussed above.

The phase diagram shown in Fig. 1 has four phase boundaries instead of three as reported in earlier work [8]. The  $u_c$  line separates the expanded and collapsed phases. This line remains straight and parallel to  $\omega$ -axis in the bulk. This result is in agreement with that of ref. [8]. The special adsorption line  $\omega_c$  separates adsorbed expanded (AE) phase from that of desorbed expanded (DE). Beyond  $\theta$ -point we have two boundaries  $\omega_{c1}$  and  $\omega_{c2}$ . The line  $\omega_{c1}$  separates the desorbed collapsed (DC) bulk phase from that of an adsorbed globule (AG) state, whereas the boundary  $\omega_{c2}$  separates the AG phase from the AE phase. The point where  $u_c$  line meets the special adsorption line  $\omega_c$ , all the four phases AE, DE, DC and AG coexist. The AG phase which exists between the boundaries  $\omega_{c1}$  and  $\omega_{c2}$  for  $u > u_c$  is essentially a two-dimensional globule sticking to the surface in the same

way as a liquid drop may lie on a surface. The existence of such a phase, to the best of our knowledge, is shown for the first time.

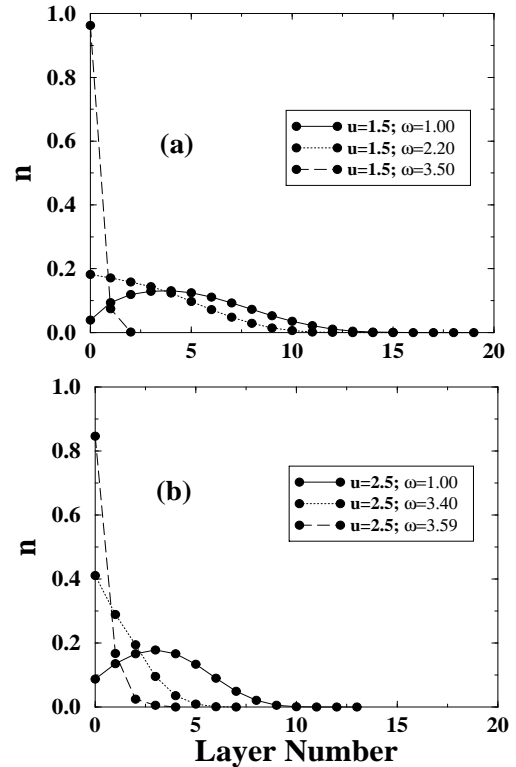


**FIG.1:** The phase diagram of a surface interacting linear polymer in 2-D space.  $\omega$  and  $u$  axes represent, respectively the Boltzmann factor of surface interaction and monomer-monomer attraction. Regions marked by AE, AG, DE and DC represent, respectively, the adsorbed polymer in expanded (swollen) state and globular state, desorbed polymer in expanded and collapsed state.

To find the monomer density as a function of distance normal to the surface for different regimes of the phase diagram we first found the terms which make most significant contribution in Eq.(1) for the walks of 26 steps. For these walks we evaluated the monomers (number of visited sites) on different lattice layers. The results are shown in Fig. 2 where we plot the fraction of monomers lying on different layers for many values of  $u$  and  $\omega$  corresponding to different parts of the phase diagram. Since the walks always start from the surface, there is at least one monomer on the surface for all the cases. In Fig. 2(a)  $u$  is taken equal to 1.5 which is less than  $u_c$  (1.93) and therefore it corresponds to expanded state. The values of  $\omega = 1.0$  and  $3.5$  correspond, respectively to DE, and AE phases, while  $\omega = 2.20$  lies on the special adsorption line  $\omega_c$  for  $u = 1.5$ . Fig. 2(b) shows the change in monomer density as  $\omega$  is increased for  $u = 2.5$ . In this case  $\omega = 1.0$ ,  $3.4$  and  $3.59$  correspond to DC, AG and AE phases, respectively. For  $u = 2.5$   $\omega_{c1} = 2.75$  and  $\omega_{c2} = 3.50$ , thus the value  $\omega = 3.59$  is just above the  $\omega_{c2}$  line. The large change in monomer density distribution when  $\omega$  value is changed from  $3.4$  (slightly below  $\omega_{c2}$  line) to  $3.59$  (just above  $\omega_{c2}$  line) is evident and confirms the existence of new (AG) phase.

In Fig. 3 we plot the quantities  $\langle n_s \rangle$  and  $\langle n_p \rangle$  giving the average fraction of monomers on the surface and number of pairs and defined as

$$\langle n_s \rangle = \lim_{N \rightarrow \infty} \frac{\partial \ln G}{\partial \omega} \Big|_u, \quad \langle n_p \rangle = \lim_{N \rightarrow \infty} \frac{\partial \ln G}{\partial u} \Big|_\omega$$

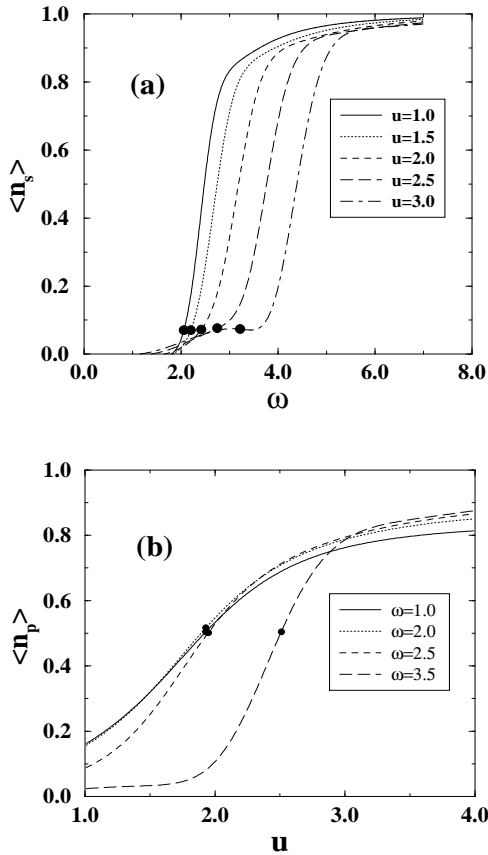


**FIG.2:** Fraction of monomers ( $n$ ) on different layer.

The transition points on each curve is marked by dot. While the dot on a curve of  $\langle n_s \rangle$  (in Fig. 3(a)) indicate the adsorption transition (*i.e* point on  $\omega_c$  and  $\omega_{c1}$  lines depending on the values of  $u$ ), the dot on a curve  $\langle n_p \rangle$  (in Fig. 3(b)) indicates the transition to collapsed state (*i.e* point on line  $u_c$  and  $\omega_{c2}$  depending on the values of  $\omega$ ). We may note that the value of  $\langle n_p \rangle$  for AG phase is comparable to that in the DC phase. We have found that along the line  $\omega_c$  and  $\omega_{c1}$ ,  $\langle n_s \rangle = 0.07 \pm 0.004$  and along the line  $u_c$  and  $\omega_{c2}$ ,  $\langle n_p \rangle = 0.5 \pm 0.003$ . This shows that the error involved in determining the phase boundaries is very small.

It is obvious from these results that when the chain gets adsorbed from the expanded bulk state (*i.e* for  $u < u_c$ ), it acquires a conformation at  $\omega \simeq \omega_c(u)$  such that a small fraction ( $\sim 10\%$ ) of monomers get attached to the surface (see Fig. 3(a)) and others are still in the bulk. Though the chain has formed a layer parallel to the surface there are considerable fluctuations in direction normal to the surface layer. As  $\omega$  is increased for the same value of  $u$ , the fluctuations along the normal to the surface get suppressed and at large  $\omega (\gg \omega_c)$  the chain lies on the surface with very little fluctuations (see Fig. 2(a)). On the other hand, when the adsorbing chain was in collapsed bulk state, then at  $\omega = \omega_{c1}$  the collapsed chain gets attached to the surface. Here again the number of monomers getting attached to the surface are about 10%

(see Fig. 3(a)). For  $\omega_{c1} \leq \omega \leq \omega_{c2}(u)$  the chain remains in the form of globule attached to the surface. In this range the monomer-monomer attraction remains effective in holding the monomers in the neighbourhood of each other than the surface-monomer attraction whose tendency is to spread the chain on the surface (see Fig. 2(b)). For  $\omega > \omega_{c2}(u)$  the globule conformation becomes unstable as surface-monomer attraction becomes more effective than the monomer-monomer attraction and therefore the chain spreads over the surface (just like a liquid spreads over a wetting surface).



**FIG.3:** (a) Average fraction of monomers on the surface ( $\langle n_s \rangle$ ) as a function of  $\omega$  and (b) number of pairs ( $\langle n_p \rangle$ ) as a function of  $u$ . Dot on a curve indicates the transition point; in (a) adsorption - desorption and in (b) expanded - collapsed transitions.

Summarizing we studied a SASAW in the presence of an attracting impenetrable wall and obtained the phase boundaries separating different phases of the polymer chain from data obtained by exact enumerations. We report a new adsorbed state which has conformation of a compact globule sticking to a surface in same way as a liquid drop may lie on a non wetting surface. The monomer density distribution, the number of monomers on the surface and the number of nearest neighbours in different regimes of the phase diagram are obtained.

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- [1] J. des Cloiseaux and G. Jannink, *Polymers in Solution* (Clarendon, Oxford) (1990); E. Eisenriegler, *Polymers Near Surfaces* (World Scientific, Singapore) (1993).
  - [2] C. Vanderzande, *Lattice Models of Polymers* (Cambridge University Press, UK) (1998); J. M. Hammersley, G. M. Torrie and S. G. Whittington, *J. Phys. A* **15** 539 (1982).
  - [3] K. Dé Bell and T. Lookman, *Rev. Mod. Phys.* **65**, 87 (1993).
  - [4] K. Kremer, *J. Phys. A*, **16**, 4333 (1983); H. W. Diehl, *Phase Transitions and Critical Phenomena*, vol. **10** edited by C. Domb and J. Lebowitz (Academic, New York), 76 (1986); E. Bouchaud E and J. Vannimenus, *J. Physique* **50**, 2931 (1989).
  - [5] P. Grassberger and R. Hegger, *Phys. Rev. E* **51**, 2674 (1995); P. Grassberger and R. Hegger, *J. Phys. I France* **5**, 597 (1995).
  - [6] H. Meirovitch and H. A. Lim, *J. Chem. Phys.* **89**, 2544 (1989); H. Meirovitch and I. S. Chang, *Phys. Rev. E* **48**, 1960 (1993).
  - [7] D. Zhao, T. Lookman and K. Dé Bell, *Phys. Rev. A* **42**, 4591 (1990).
  - [8] D. P. Foster, E. Orlandini and M. C. Tesi, *J. Phys. A: Math. Gen.* **25**, L1211 (1992).
  - [9] M. T. Batchelor and C. M. Yung, *Phys. Rev. Lett.* **74**, 2026 (1995).
  - [10] P. G. de Gennes, *Scaling Concepts in Polymer Physics* (Cornell Univ. Press, Ithaca, 1979); *J. Phys. (Paris)* **36**, 155 (1975).
  - [11] T. Ishinabe, *J. Chem. Phys.* **76**, 5589 (1982); *J. Chem. Phys.* **77**, 3171 (1982); *J. Chem. Phys.* **80**, 1318 (1984); C. Vanderzande, A. L. Stella and F. Seno, *Phys. Rev. Lett.* **67**, 2757 (1991).
  - [12] D. P. Foster and J. Yeomans, *Physica A* **177** 443 (1991); F. Igloi, *Phys. Rev. A* **43**, 3194 (1991).
  - [13] T. Vrbová and S. G. Whittington, *J. Phys. A: Math Gen.* **31**, 3989 (1998).
  - [14] Y. Singh, S. Kumar and D. Giri, *J. Phys. A: Math Gen.* **32**, L407 (1999).
  - [15] D. S. Gaunt and A. J. Guttmann, *Phase Transitions and Critical Phenomena*, edited by C. Domb and M. S. Green (Academic, London), **Vol. 3** (1974).